Changes in Thermal Diffusivity of Rubber Due to Mechanical Preconditioning

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Introduction

The mechanical response of elastomers becomes consistent only after thermomechanical preconditioning, needed to break temporary intermolecular cross-links [1]. Two methods of preconditioning are often used, static and cyclic. Static preconditioning requires stretching the elastomer beyond the maximum stretch that is to be tested and maintaining this stretch until the load has relaxed to some asymptotic value. Cyclic preconditioning stretches the specimen to its maximum test stretch repeatedly until the mechanical response curves are consistent. For each preconditioning protocol, the temperature of the specimen is maintained at or above the testing temperature. Uniaxial stretch has been found to change the thermal conductivity of nitrile and natural rubber at temperature to 100 K [2]. Recent measurements reveal changes in the thermal diffusivity of neoprene rubber undergoing finite biaxial deformation at room temperature [3]. These measurements revealed that the thermal diffusivity changes with preconditioning. How these thermal diffusivities changed with time after preconditioning was not revealed, nor whether the properties of the native material were recovered. Furthermore, only cyclic preconditioning was considered for the neoprene.

Here, changes to the out-of-plane component of the thermal diffusivity tensor due to mechanical preconditioning are examined. Two room temperature vulcanizing (RTV) rubbers, silicone and polyurethane (PU) are tested. The silicone rubber is subject to cyclic preconditioning while the PU rubber is subject to both cyclic and static preconditioning. The thermal and mechanical responses of the materials are examined.

Methods and Materials

The flash device incorporating computer controlled finite deformation is described in detail elsewhere [3]. Briefly, the optical-thermomechanical system consists of two subsystems: a) a biaxial loading and in-plane strain measurement system and b) a flash illumination and point-wise temperature measurement system.

Biaxial loading and in-plane strain measurement. This subsystem consists of a load frame and four load carriages that apply nearly uniformly distributed in-plane biaxial loading to a square specimen attached to the carriages using Kevlar threads. Two perpendicular carriages are equipped with watertight, temperature compensated load cells, and each carriage is driven by a computer-controlled stepper-motor. The in-plane finite strains are measured optically using a CCD video camera, frame-grabber board in a PC, and custom software capable of tracking at 30 Hz the position of four small contrasting markers (80-100 μm) that are glued to the bottom surface of the specimen. A bilinear isoparametric interpolation algorithm uses the marker positions to calculate the components of the deformation gradient tensor $\mathbf{F}$ in the central region [4], which are then used as control parameters of the automated motor control system. The load carriages are enclosed by an environmental chamber with a temperature controller heater that allows testing at nearly constant temperature (± 1 °C). The signals from the two load cells are recorded by an eight channel, 16 bit A/D board in the PC with a sampling rate of 10 to 325 Hz.

Flash system and temperature measurement The principle of the flash technique for measuring thermal diffusivity is described elsewhere (see, for example, [6-10]). Briefly, the flash system consists here of a linear xenon flashtube, mounted in an aluminum reflector, that delivers a short burst of energy to the 40 mm square top surface of the specimen. The temperature history of the bottom face of the specimen is measured using a 0.25 mm diameter E-Type thermocouple mounted to a micrometer head so that it can be brought in contact with the specimen. A small amount of high thermal conductivity paste is used to reduce contact resistance. A T-Type thermocouple measures the temperature in the environmental chamber near the specimen and another signals the flash event on the computer file. The thermocouple signals are also recorded using the A/D board.

Specimen preparation Silicone and polyurethane (PU) based room temperature vulcanizing (RTV) rubber liquid kits (Polytek Development Corp.) were prepared according to manufactures instructions. After mixing, the mixtures were de-aerated under a vacuum of about 96 kPa for 10 minutes to obtain a bubble-free specimen. Fifteen grams of the mixture was poured into each of two aluminum molds of 57x57x8 mm and 63x63x5 mm, respectively. Two jigs, each containing 24 uniformly distributed 1.30 mm diameter glass rods were placed and fixed to the upper surface of each mold. The molds were placed to a temperature controlled curing chamber at 20 °C and left to cure for 24 hours. The jigs and glass rods were then removed and the specimens taken from the mold and placed in a tray at least one week before testing. Two specimens are obtained from each mixing cycle with thickness varying from 3.25 to 3.8 mm.

Before testing, all specimens were cleaned with distilled water and carefully measured. The native thickness of the specimen was calculated by averaging the distribution obtained by measuring the thickness at 25 points in a staggered grid pattern using a micrometer. Sleeves of 1.6 mm diameter and 4.8 mm long were placed in the specimen orifices left by the glass rods and glued with a cyanoacrylate-based glue. The cyanoacrylate is far from the central region where the deformation and diffusivity were measured. The four 75 to 90 μm contrasting microspheres were then placed in the central region of the specimen surface in order to measure the in-plane stretch during and after preconditioning.

Preconditioning protocol testing Initial mechanical tests characterized the most suitable mechanical preconditioning protocols for the silicone RTV. These tests consisted of a finite number of equibiaxial loading and unloading cycles up to a maximum predefined stretch λ_{max}. Cyclic tests with silicone to $\lambda_{max} > 1.5$ produced premature failure of the specimens at the loading points, cracks first appearing between the sleeves and rubber and propagating to neighboring load points until the specimen failed completely. Similarly, equibiaxial static preconditioning was tested. This protocol consisted of a continuous equibiaxial stretch for 24 hours at a selected λ at room temperature. Specimens remained intact only for static preconditioning with $\lambda \leq 1.2$. This low value of stretch limited too greatly the maximum stretch that could be applied during diffusivity measurement. Therefore, equibiaxial cyclic preconditioning was used for the silicone specimens, the protocol consisting of 5 cycles at $\lambda = 1.2$, followed by 15 cycles at $\lambda = 1.4$.

Figure 1 shows typical results of the cyclic equibiaxial preconditioning with $\lambda = 1.4$ for the silicone. The stress-stretch curves 9 and 10 are nearly indistinguishable and more compliant than the first cycle. This indicates that the specimen is preconditioned after 9 cycles, though 15 cycles are used to insure preconditioning. Furthermore, if a specimen is left to relax for 24 hours, it partially recovers to its native state, but the preconditioned response is recovered quickly after the second cycle of a re-applied preconditioning.

Different cyclic preconditioning protocols were examined for PU based rubber specimens, which better resist tearing than do the silicone ones. Specimens withstood equibiaxial stretch up to $\lambda = 2.2$ (the maximum possible stretch with the current device) with no cracks at the loading points such as those that compromised the integrity of the silicone specimens. Comparing in-plane Cauchy stress ($t_{11} = t_{22}$) — stretch curves for different cycles showed that the specimens were well preconditioned after 18 cycles suggesting a cyclic preconditioning protocol for PU of 5 cycles at λ=1.4 followed by 20 cycles with $\lambda = 2.0$. The response is similar to that of Fig. 1 if cycles 1, 19, and 20 are substituted. Since PU exhibits good resistance to damage during cyclic preconditioning protocols, static equibiaxial static preconditioning protocols were also examined. Relaxation response curves for the PU specimens showed that the in-plane stresses were independent of time after 41 hours (Fig. 2), suggesting a static protocol for PU of 48 hours at λ =1.8 and room temperature.

Cyclic mechanical testing performed immediately after preconditioning showed that specimens were preconditioned well with repeatable stress-stretch curves on the first and second cycle. Tests performed 24 hours after preconditioning showed that PU undergoes a partial recovery to its unpreconditioned mechanical state, requiring 15 cycles to achieve its preconditioned state for PU specimens preconditioned cyclically and 8 cycles for those statically preconditioned.

Thermal Diffusivity Measurements Three silicone and four PU specimens were selected from those prepared as described above. The thicknesses for the native silicone specimens were 3.473, 3.461 and 3.450 mm with standard deviations of 0.013, 0.012 and 0.007 mm, respectively. Similarly, the thicknesses for the native PU specimens were 3.812, 3.213, 3.196 and 3.199 mm with standard deviation of 0.011, 0.009, 0.005 and 0.007mm, respectively.

Each specimen was secured into the computer controlled multi-axial finite-deformation loading system described above. The out-of-plane component of $\overline{\alpha}$ was measured using the flash technique [6] following ASTM standard E-1461-92 [10]. Briefly the method consists of exposing the specimen with a short burst of radiant energy, here using a Xe flash lamp, that heats the front face of the specimen while recording the temperature history of the rear face. Data reduction is accomplished by using $\alpha_{33} = c_x \delta^2 / \tau_x$, where δ is the thickness of the specimen and t_x is the time needed for the rear-face temperature to reach a fraction x of its maximum temperature $T_{\max}$. For $x = 0.25$, 0.50, and 0.75 of $T_{\max}$, c_x is 0.09225, 0.13879

and 0.21049, respectively [10]. In addition, a Levenberg-Marquardt parameter estimation algorithm [12] coupled with a finite difference model of the 1-D heat diffusion equation was employed as an alternative data reduction. This permitted the inclusion of more realistic boundary condition, such as possible convective losses and finite duration light pulse. The algorithm minimized the sum of squares of the difference between the temperature calculated by the numerical model and the measured temperature history to optimize the estimated value of α_{33}. The algorithm estimated the heat flux per unit area, the convective heat transfer coefficient (which matched well convection correlations), and α_{33}.

Each specimen was subjected to eight pulses to determine α_{33} at its native state; the pulses were separated by 15 minutes to allow the specimen to regain thermal equilibrium. The unloaded reference configuration of the specimen was registered by recording the position of the markers at the surface of the specimen. The chosen preconditioning protocol was then applied to the specimen and the unloaded configuration was registered immediately after preconditioning to determine if any deformation remained in the specimen. Thickness measurements after preconditioning were calculated using the specimen native thickness, the in-plane deformation, and assuming mechanical incompressibility ($|\mathbf{F}| = 1 = \lambda_1 \cdot \lambda_2 \cdot \lambda_3$ where λ_1 and λ_2 are the in-plane stretches and λ_3 the out-of-plane stretch). Mechanical incompressibility was verified experimentally for PU and silicone for equibiaxial stretch up to $\lambda = 1.8$ and $\lambda = 1.2$, respectively.

For the specimens cyclically preconditioned (1, 2, 3, and 4) two sets of ten pulses with 15 minutes between pulses, one starting at 15 minutes and the other 24 hours after preconditioning, were applied, carefully recording at the beginning of each set the unloaded configuration so as to determine δ. Specimen 5 (PU) was subjected to a set of ten pulses after cyclic preconditioning, followed by static preconditioning and α_{33} measurements at 2, 18, 27, 41, and 65 hours after the last preconditioning protocol. Specimens 6 and 7 (PU) were statically preconditioned and subjected to consecutive pulses at approximately 20 minutes intervals for eight hours, carefully recording the specimen unloaded configuration every three pulses. Following that, a set of five pulses at 20 minute intervals were applied to the specimen at 24 hours after preconditioning.

Cyclic preconditioning was applied to all specimens, both statically and cyclically preconditioned, after α_{33} measurement and approximately 24 hours after initial preconditioning, to evaluate the mechanical state.

Results

Table 1 shows the effect of the cyclic preconditioning on α_{33} for the silicone and PU specimens obtained by performing 1-D flash tests to the specimens at their unloaded state, before preconditioning and at 15 minutes and 24 hours after preconditioning. Thickness measurements before and after the preconditioning showed that there were no residual deformation effects for the silicone specimens. There was a small residual in-plane deformation of approximately λ=1.04 for PU specimens, with no change in the volume.

Cyclic preconditioning causes an immediate increase of 5.2 and 4.0% in α_{33} for the silicone and PU specimens, respectively. Twenty four hours after such preconditioning α_{33} decreases to about 2% higher than the native states for the silicone and PU specimens. These results suggest a partial recuperation of their native state, which is consistent with the results of mechanical tests performed 24 hours after preconditioning for which stress-stretch curves show that the materials recover partially their native state. Further mechanical tests showed that the preconditioned mechanical response is quickly recovered after 2 and 15 cycles of re-applied preconditioning for the silicone and PU specimens, respectively.

Figure 4 shows α_{33} of PU specimens after 48 hours of equibiaxial static preconditioning at $\lambda = 1.8$. Specimen 5 had previously been subjected to cyclic preconditioning, as discussed above and had consequently an initial deformation Immediately after preconditioning, $\lambda_1 = \lambda_2 = 1.10$ at the unloaded state; this decreased to $\lambda_1 = \lambda_2 = 1.05$ after 8 hours remaining at this value for at least 70 hours after preconditioning. For specimens 6 and 7, α_{33} increases 20 to 25% immediately after preconditioning, followed by a decrease to within 3 to 11% of the native value for PU following 24 hours. After the static preconditioning, α_{33} of specimen 5 increases to about 38% greater than its native value, but this is only a 25% increase from its value after the cyclic preconditioning (represented in the figure by the dash line). Tests performed to specimen 5 from 27 to 114 hours after preconditioning show that α_{33} reaches an asymptote with respect to time at a value that slightly greater than α_{33} before the static preconditioning.

Discussion

Measurements show that preconditioning increases α_{33} for PU and silicone and that this increase is smaller for specimens undergoing cyclic preconditioning as compared with static preconditioning. There is an increase in α_{33} immediately after preconditioning followed by a slower decrease in α_{33} as the material recovers to nearly its native state. Permanent in-plane deformation for PU suggests that the permanent change of α_{33} from its native value is due to the permanent in-plane deformation due to broken cross links or by partial crystallization of the material. In contrast, the lack of temporary deformation observed in the silicone after preconditioning and the amorphous structure of silicone suggest that these changes are best explained by changes at the molecular level.

General thermoelastic analysis of elastomeric materials must take into account the changes that preconditioning produces in its thermal properties and how these evolve with relaxation with material. Furthermore, studies should be performed to determine the effect of preconditioning on the in-plane components $\overline{\alpha}$ and their evolution as the material relaxes from its preconditioned state. Ortt *et al.* [3] demonstrated that the in-plane components of diffusivity of neoprene decrease with cyclic preconditioning but did not explore the relaxation history or compare cyclic with static preconditioning. Because this is the plane of the most deformation and it might be expected to encounter greater intermolecular changes are revealed in thermal diffusivity.

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Table 1. Effect of cyclic precondition on α_{33}.

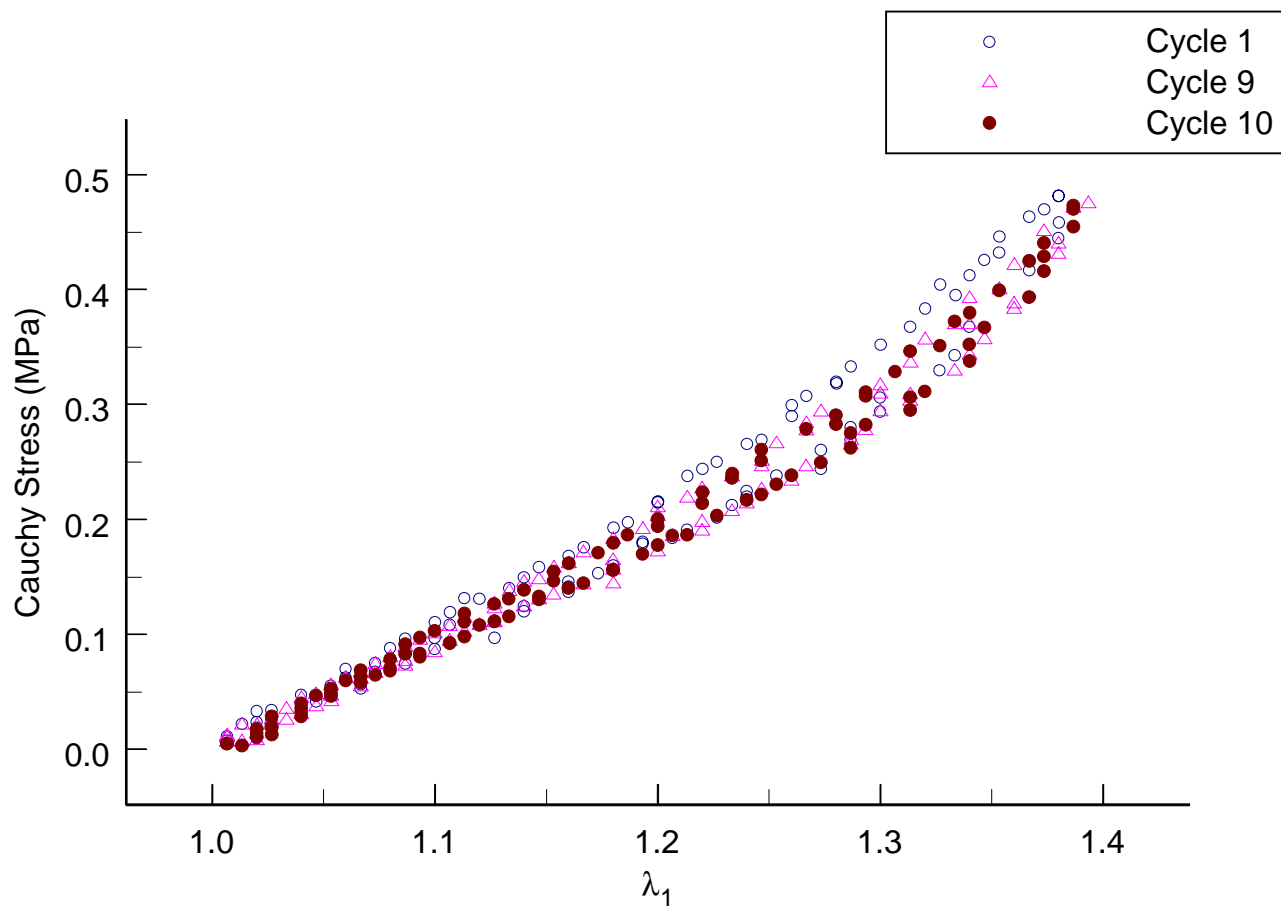| specimen	material	$\alpha_{33} \pm$ stdv (10^7 m^2/s)		
		Native	15min. after precondition	24 hours after precondition
1	Silicone	1.256 ± 0.024	1.349 ± 0.020	1.300 ± 0.030
2	Silicone	1.249 ± 0.045	1.354 ± 0.026	1.345 ± 0.017
3	Silicone	1.275 ± 0.006	1.330 ± 0.021	1.261 ± 0.064
Average Silicone		1.278 ± 0.014	1.344 ± 0.013	1.303 ± 0.042
4	PU	0.809 ± 0.010	0.836 ± 0.008	0.824 ± 0.010
5	PU	0.765 ± 0.017	0.798 ± 0.007	N/A
Average PU		0.787 ± 0.031	0.817 ± 0.027	0.824 ± 0.010

Figure 1. Cyclic preconditioning response of silicone RTV rubber
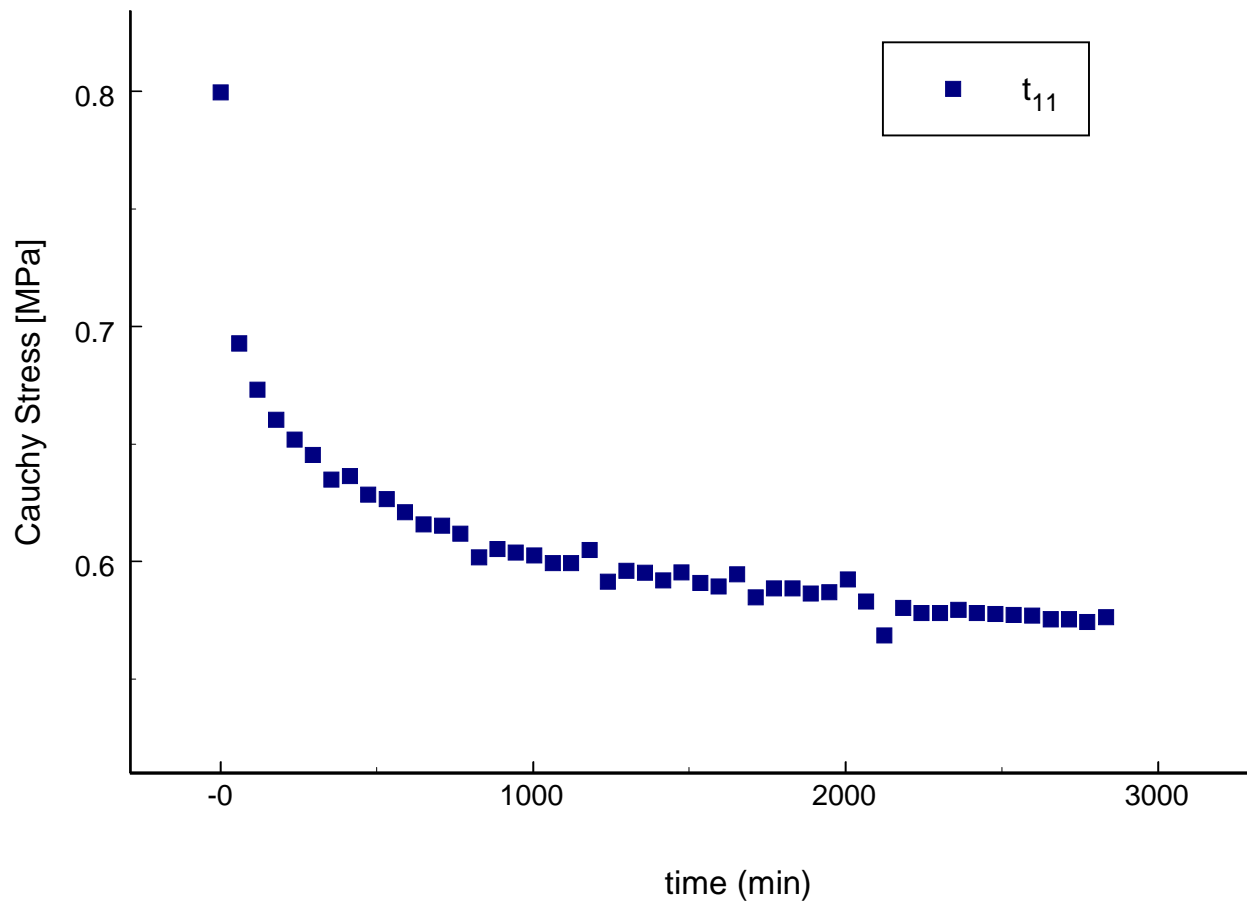
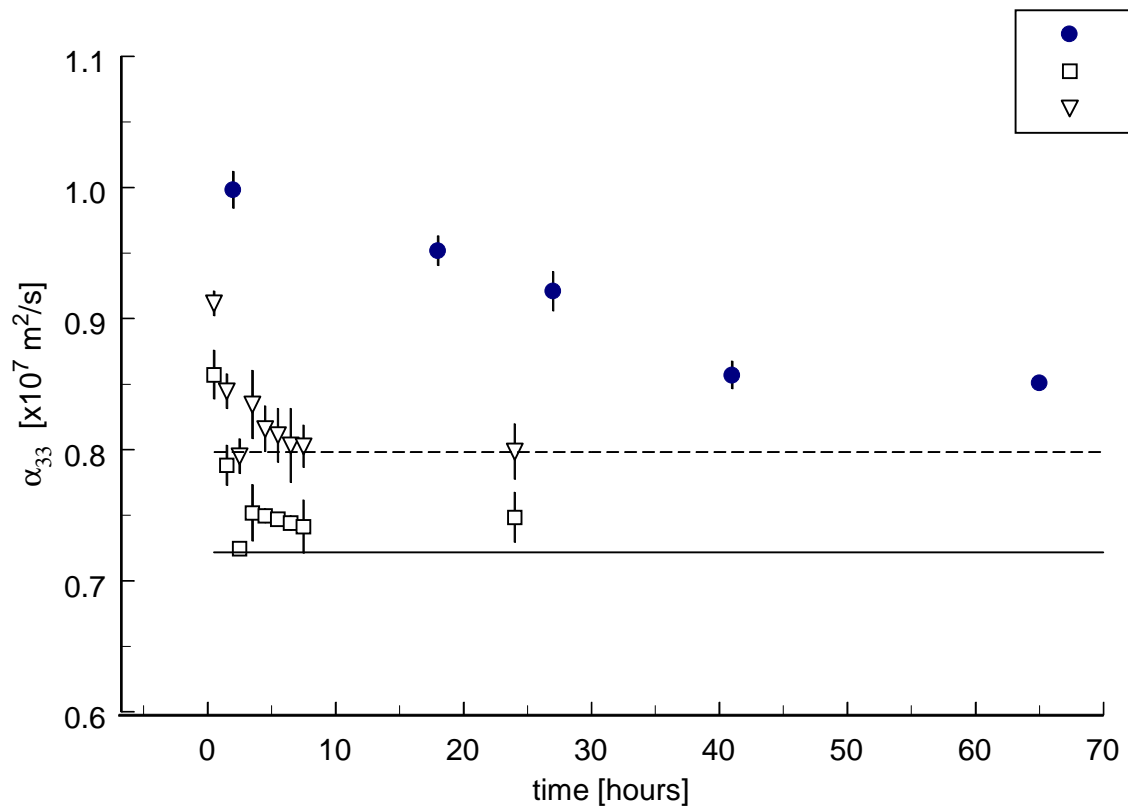Figure 2. Stress relaxation of PU rubber specimen maintained at $\lambda = 1.8$.

Figure 3. Thermal diffusivity of PU rubber after preconditioning.